

## TITLE

### BIOMEDICAL SUPERELASTIC Ti-BASED ALLOY, ITS PRODUCT AND ITS MANUFACTURING METHOD

#### Technical Field

5           The present invention relates to superelastic Ti-based alloy, and more particularly, to biomedical superelastic Ti-based alloy optimal for medical appliances or the like, its products and its manufacturing method.

#### Related Art

10           In recent years, alloys provided with superelastic characteristic have been used in medical fields. For example, Ti-Ni has properties of high strength, excellent abrasion resistance, good corrosion resistance, good biocompatibility, etc. and therefore, has been used in various fields as temporary or semi-permanent biomedical materials.

          However, with respect to biomedical materials using an alloy including Ni, it is feared that the Ni element presumed to contribute to allergic symptoms dissolves in the human body.  
15           Ti-Ni based alloy with Ni as a principal element has a possibility of causing a human to have allergic symptoms, and is assumed not to be preferable. Therefore, demands have been increasing for safer superelastic alloy without containing an element causing a human to be poisoned or allergic.

          Fig.4 shows a result of a survey on effects of various pure metallic elements on a human  
20           body. Specifically, FIG.4 shows a result of the survey on effects of various pure metallic elements on a human body where the horizontal axis indicates the cell growth coefficient of chick embryo myocardial osteoblastic tissue and the vertical axis indicates the relative proliferation rate of L929 cell derived from mouse fibroblastic tissue (refer to Materials Science and Engineering A, A243, pages 244 to 249, 1998). The figure indicates that V, Cd, Co, Cu, Zn  
25           and Hg are elements high in cytotoxicity, and that Zr, Ti, Nb, Ta, Pd and Au are excellent in biocompatibility.

          Further, FIG.5 shows a result where the horizontal axis indicates the biocompatibility and the vertical axis indicates the polarization resistance ( $R/\Omega \cdot m$ ) as an index of corrosion resistance

in a human body(refer to the same as in FIG.4). The figure indicates that Pt, Ta, Nb, Ti and Zr are high in polarization resistance, and therefore, low in solubility in a human body and excellent in biocompatibility.

Japanese Laid-Open Patent Publication No.2001-329325 discloses using Ti-Nb-Sn alloy comprised of elements excellent in biocompatibility as a biomedical shape memory and superelastic alloy.

Ni-Ti alloy that is conventionally used as a biomedical superelastic alloy material has the Ni element assumed to contribute to allergic symptoms, and so, has a fear of effects on a human body. Therefore, it is desired to develop a superelastic alloy material comprised of elements excellent in biocompatibility. However, an alloy material provided with superelastic characteristic capable of resisting practical use has not been developed yet.

In view of the foregoing, the present invention intends to provide a biomedical alloy which has a composition without an element having concerns about human allergy such as Ni, is high in biocompatibility and has superelasticity because superelastic alloys with higher biocompatibility are desired.

The Ti-based alloy has a small residual deformation strain in a certain composition after undergoing solution treatment, i.e., obtains the superelasticity. However, conventionally available materials with superelasticity have a smaller limitation strain that represents the superelasticity than that of Ti-Ni based alloy, and are not sufficient for use in biomedical appliances. As a cause, it is considered that the heat solution treatment decreases a critical stress for slip deformation, and it is considered that a permanent strain appears due to slip deformation greater than limitations where complete superelasticity develops.

In order to increase the critical stress for slip deformation, a method is considered of causing fine precipitates that prevent slip deformation. Ti-Nb-Sn based alloy is subjected to artificial aging after undergoing the heat solution treatment to cause  $\omega$ -phase to be precipitated, thereby obtaining the superelasticity. However, increasing the precipitation of  $\omega$ -phase causes the alloy to be too much brittle, and therefore, controlling the precipitation of  $\omega$ -phase obtains superelasticity only to some extent.

Further, in order to increase the critical stress for slip deformation, a method is considered of providing a worked structure resistant to slip deformation. Ti-based alloy is subjected to the final cold-working with a processing rate of a predetermine value or more, and is

subjected to the heat treatment at a predetermined temperature, and thus the superelasticity is obtained. In this method, since the heat treatment is carried out at a relatively high temperature so as to prevent the  $\omega$ -phase from being precipitated, the critical stress for slip deformation is low, and it is not possible to obtain the superelasticity of a level required for practical use.

5           Accordingly, the present invention intends to develop and provide biomedical superelastic Ti-based alloy with excellent superelasticity using an alloy with a predetermined composition, and a method of manufacturing such an alloy.

#### Disclosure of Invention

10           In order to overcome aforementioned issues, a first embodiment of the present invention is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb that is an element for stabilizing  $\beta$ -phase of Ti, and comprising Ti and unavoidable impurities as the residual part.

A second embodiment of the present invention is the biomedical superelastic Ti-based alloy with a composition having:

- 15           (a)     one or more elements selected from the group consisting of 10at % or less of Mo, 15at % or less of Al, 10at % or less of Ge, 10at % or less of Ga, and 15at % or less of In;
- (b)     30 at % or less of a sum total of the one or more elements selected from the group consisting of Mo, Al, Ge, Ga, and In;
- (c)     60 at % or less of a sum total of Nb and the one or more elements selected from the group consisting of Mo, Al, Ge, Ga, and In; and
- 20           (d)     Ti and unavoidable impurities as the residual part.

A third embodiment of the present invention is the biomedical superelastic Ti-based alloy with a composition having:

- (a)     one or more elements selected from the group consisting of 7 at % or less of Mo, 10at % or less of Al, 6 at % or less of Ge, and 6 at % of Ga;
- 25           (b)     60 at % or less of a sum total of Nb and the one or more elements selected from the group consisting of Mo, Al, Ge, and Ga; and
- (c)     Ti and unavoidable impurities as the residual part.

A fourth embodiment of the present invention is the biomedical superelastic Ti-based alloy with a composition having:

- (a) one or more elements selected from the group consisting of 10at % or less of Mo, 15at % or less of Al, 10at % or less of Ge, 10at % or less of Ga, and 15at % or less of In;
- (b) 15at % or less of Sn;
- (c) 30at % or less of a sum total of the one or more elements selected from the group consisting of Mo, Al, Ge, Ga, and In, and Sn;
- (d) 60at % or less of a sum total of Nb, the one or more elements selected from the group consisting of Mo, Al, Ge, Ga and In, and Sn; and
- (e) Ti and unavoidable impurities as the residual part.

A fifth embodiment of the present invention is the biomedical superelastic Ti-based alloy with a composition having:

- (a) one or more elements selected from the group consisting of 7 at % or less of Mo, 10at % or less of Al, 6 at % or less of Ge, and 6 at % or less of Ga;
- (b) 12 at % or less of Sn;
- (c) 60 at % or less of a sum total of Nb, the one or more elements selected from the group consisting of Mo, Al, Ge and Ga, and Sn; and
- (d) Ti and unavoidable impurities as the residual part.

In a sixth embodiment of the present invention, the alloy is a biomedical superelastic Ti based apply for use in either of a medical guide wire, orthodontic wire, stent, actuator of an endoscope, eyeglass frame, and nose pad arm of eyeglass.

A seventh embodiment of the present invention is a medical guide wire using the biomedical superelastic alloy.

An eighth embodiment of the present invention is an orthodontic wire using the biomedical superelastic alloy.

A ninth embodiment of the present invention is a stent or an actuator of an endoscope using the biomedical superelastic alloy.

A tenth embodiment of the present invention is an eyeglass frame or a nose pad arm of eyeglass using the biomedical superelastic alloy.

An eleventh embodiment of the present invention is an actuator of an endoscope using the biomedical superelastic alloy.

A twelfth embodiment of the present invention is a method of manufacturing a biomedical superelastic alloy for preparing an ingot comprising a Ti-based alloy containing Ti

and Nb as an essential component, or the Ti-based alloy further containing one or more elements of Mo, Al, Ge, Ga and In and unavoidable impurities as the residual part, performing hot-working and cold-working on the ingot, performing annealing subsequent to the cold-working and further final cold-working with a processing rate of 20% or more, and performing heat  
5 treatment at a temperature of 300°C or more so as not to cause recrystallization or enlargement of crystal particle due to recrystallization.

A thirteen embodiment of the present invention is the method of manufacturing a biomedical superelastic Ti-based alloy, where the Ti-based alloy has 10 to 40at % of Nb as an essential component, one or more elements selected from the group consisting of 10at % or less  
10 of Mo, 15at % or less of Al, 10at % or less of Ge, 10at % or less of Ga, and 15at % or less of In, 30at % or less of a sum total of the one or more elements selected from the group consisting of Mo, Al, Ge, Ga and In, 60at % or less of a sum total of Nb as the essential element and the one or more elements selected from the group consisting of Mo, Al, Ge, Ga, and In, and Ti and unavoidable impurities as the residual part.

15 A fourteenth embodiment of the present invention is the method of manufacturing a biomedical superelastic Ti-based alloy where in the heat treatment, heating temperature ranges from 400 to 500°C, and heating time ranges from 1 minute to 2 hours.

A fifteenth embodiment of the present invention is the method of manufacturing a biomedical superelastic Ti-based alloy where in the heat treatment, heating temperature ranges  
20 from 400 to 500°C, heating time ranges from 1 minute to 2 hours, and residual strain is 1.5% or less after loading up to 4% strain.

#### Brief Description of Drawings

Fig.1 is a view to explain a method of measuring a curve angle;

Fig.2 shows a stress-strain curve of an example of the present invention;

25 Fig.3 shows a stress-strain curve of a comparison example;

Fig.4 is a graph illustrating cytotoxicity of pure metals;

Fig.5 is a graph illustrating the relationship between polarization resistance and biocompatibility of pure metals, etc; and

Fig.6 is a schematic view illustrating a state of development of superelasticity.

## Detailed Description of the Preferred Embodiments

### (First embodiment)

The first embodiment of the present invention will be described below. In order to cause martensite of Ti-based alloy to be thermo elastic, the alloy of this embodiment is a Ti-based alloy to which is added Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature. In other words, the alloy of this embodiment is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb that is an element for stabilizing  $\beta$ -phase of Ti, and Ti and avoidable impurities as the residual part.

The conventional Ti-Ni based alloy is the so-called shape memory alloy, and has the so-called shape memory effect that an alloy in a certain shape is transformed into another shape different from the original shape at a low temperature, and when being heated at a temperature or more such as a high-temperature phase (base phase in this case) is stabilized, returns to the shape of before being transformed due to inverse transformation (phase transformation occurring due to heat and unloading).

While all the alloys causing martensitic transformation do not always have the shape memory effect, alloys causing thermo-elastic martensitic transformation (including Ti-Ni based alloy) have characteristics of returning to the original shape almost perfectly by heating when the transformation level is within certain limitations. The alloy of this embodiment is a Ti-based alloy provided with such characteristics.

In order to cause martensite of Ti-based alloy to be thermo elastic, the Ti-Nb based alloy of the present invention has Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature. By adding Nb that is an element for stabilizing  $\beta$ -phase of Ti, the temperature of  $\alpha/\beta$ -phase transformation point shifts to a lower temperature, and it is possible to obtain the alloy with stabilized  $\beta$ -phase even at room temperature. In other words, cooling the  $\beta$ -phase region rapidly enables the  $\beta$ -phase to remain. It is known that an alloy with approximately 20 at % or less of Nb causes martensitic transformation even when cooled rapidly, and that the  $\beta$ -phase does not remain thoroughly.

Two kinds of martensites,  $\alpha'$ -phase and  $\alpha''$ -phase, exist, and as a crystal structure, the  $\alpha'$ -phase is hexagonal, while the  $\alpha''$ -phase is orthorhombic. In order to cause the superelastic effect to develop, it is necessary to make the martensitic transformation thermo-elastic, and it is known that the  $\alpha''$ -phase can be thermo-elastic among the two martensites.

In this embodiment, to cause the superelasticity to develop, the content of Nb is 5 to 40 at %. This is because the content of less than 5at % or more than 40at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state. The Ti-based alloy containing 5 to 40 at % of Nb becomes  $\beta$ -phase solid-  
5 solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working, and lower in processing cost than Ti-Ni based alloy.

(Second embodiment)

10 The second embodiment of the present invention will be described below. An alloy of this embodiment is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb that is an element for stabilizing  $\beta$ -phase of Ti, one or more elements selected from among 10 at % or less of Mo, 15 at % or less of Al, 10at % or less of Ge, 10at % or less of Ga, and 15at % or less of In, and Ti and unavoidable impurities as the residual part, where the sum total of one or more  
15 elements selected from among Mo, Al, Ge, Ga, and In is 30 at % or less, and the sum total of Nb and one or more elements selected from among Mo, Al, Ge, Ga, and In is 60 at % or less.

In this embodiment, to cause the superelasticity to develop, the content of Nb is 5 to 40 at %. This is because the content of less than 5 at % or more than 40 at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to  
20 the original state. The Ti-based alloy containing 5 to 40at % of Nb becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working .

The reason for adding Nb and one or more elements selected from among Mo, Al, Ge, Ga  
25 and In to Ti is to make the superelasticity stable and excellent. Mo is an element which stabilizes  $\beta$ -phase and decreases the martensitic transformation temperature, as well as Nb. Added Al, Ge, Ga or In serves as an element for stabilizing  $\alpha$ -phase.

In this embodiment, the content of Nb is 5 to 40at %, the content of Mo is 10at % or less, the content of Al is 15at % or less, the content of Ge is 10at % or less, and the content of Ga is  
30 10at % or less. Exceeding the ranges degrades the superelasticity. In is added to improve the

workability in an amount of 15at % or less. In an amount exceeding 15at % causes the superelasticity not to develop.

In this embodiment, the sum total of one or more elements selected from among Mo, Al, Ge, Ga, and In is 30 at % or less, and the sum total of Nb and one or more elements selected from among Mo, Al, Ge, Ga, and In is 60 at % or less. This is because the workability deteriorates when the sum total exceeds 30 at % of one or more elements selected from among Mo, Al, Ge, Ga, and In. Further, the superelasticity deteriorates when the sum total exceeds 60 at % of Nb and one or more elements selected from among Mo, Al, Ge, Ga, and In.

The Ti-Nb-Mo based alloy of this embodiment will be described below. When adding Mo that is an element for stabilizing  $\beta$ -phase to a Ti-Nb based alloy, the temperature of  $\alpha/\beta$ -phase transformation point shifts to a lower temperature, and it is possible to obtain the alloy with stabilized  $\beta$ -phase even at room temperature. In other words, cooling the  $\beta$ -phase region rapidly enables the  $\beta$ -phase to remain.

In this embodiment, the content of Mo is limited to a range of 10at % or less. The reason for the range is because the content exceeding 10at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 10at % or less of Mo becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working, and lower in processing cost than Ti-Ni based alloy.

The Ti-Nb-Al based alloy of this embodiment will be described below. When Al is added to Ti, it is considered that Al serves as an element for stabilizing  $\alpha$ -phase, the  $\alpha$ -phase region expands, and that the strength at RT increases. Therefore, in a composition with Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature and Al that is an element for stabilizing  $\alpha$ -phase, the martensite developing due to rapid cooling becomes thermo-elastic, thus obtaining  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity.

In this embodiment, the content of Al is 15at % or less. This is because the content exceeding 15at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.



Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 15at % or less of Al becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working and lower in processing cost than Ti-Ni based alloy.

The Ti-Nb-Ge based alloy of this embodiment will be described below. When Ge is added to Ti, Ge serves as an element for stabilizing  $\alpha$ -phase. In this embodiment, the content of Ge is 10at % or less. This is because the content exceeding 10at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 10at % or less of Ge becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working , and lower in processing cost than Ti-Ni based alloy.

The Ti-Nb-Ga based alloy of this embodiment will be described below. When Ga is added to Ti, Ga serves as an element for stabilizing  $\alpha$ -phase. In this embodiment, the content of Ga is 10at % or less. This is because the content exceeding 10at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 10at % or less of Ga becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working , and lower in processing cost than Ti-Ni based alloy.

The Ti-Nb-In based alloy of this embodiment will be described below. When In is added to Ti, In serves as an element for stabilizing  $\alpha$ -phase. In this embodiment, the content of In is limited to a range of 15at % or less. This is because the content exceeding 15at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 15at % or less of In becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is easy in hot-working and cold-working , and lower than in processing cost than Ti-Ni based alloy.

The Ti-Nb-Mo-Al-Ga based alloy of this embodiment will be described below. When adding Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature, Mo that is an element for stabilizing  $\beta$ -phase and Al and Ga that serve each as an element for stabilizing  $\alpha$ -phase to Ti, the temperature of  $\alpha/\beta$ -phase transformation point shifts to a lower temperature, and it is possible to obtain the alloy with stabilized  $\beta$ -phase even at room temperature. In other words, cooling the  $\beta$ -phase region rapidly enables the  $\beta$ -phase to remain.

To cause the superelasticity to develop, the content of Nb is 5 to 40at %. This is because the content of less than 5at % or more than 40at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

The content of Mo is 10at % or less. This is because the content exceeding 10at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

The content of Al is 15at % or less. This is because the content exceeding 15at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

The content of Ga is 10at % or less. This is because the content exceeding 10at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb, 10at % or less of Mo, 15at % or less of Al, and 10at % or less of Ga becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working , and lower in processing cost than Ti-Ni based alloy.

(Third embodiment)

The third embodiment of the present invention will be described specifically below. An alloy of this embodiment is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb, one or more elements selected from among 7at % or less of Mo, 10at % or less of Al, 6at % or less of Ge, and 6at % or less of Ga, and Ti and unavoidable impurities as the residual part, where the sum total of Nb and one or more elements selected from among Mo, Al, Ge, and Ga is 60at % or less.

In this embodiment, to cause the superelasticity to develop, the content of Nb is 5 to 40at %. This is because the content of Nb less than 5at % or more than 40at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does not return to the original state. The Ti-based alloy containing 5 to 40at % of Nb becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working .

The reason for adding Nb and one or more elements selected from among Mo, Al, Ge, and Ga to Ti is to make the superelasticity stable and excellent. Mo is an element which stabilizes  $\beta$ -phase and decreases the martensitic transformation temperature, as well as Nb. Added Al, Ge, or Ga serves as an element for stabilizing  $\alpha$ -phase.

In this embodiment, to improve the workability, the content of Mo is 7at % or less, the content of Al is 10at % or less, the content of Ge is 6at % or less, and the content of Ga is 6at % or less.

In this embodiment, the sum total of Nb and one or more elements selected from among Mo, Al, Ge, and Ga is 60 at % or less. This is because the superelasticity deteriorates when the sum total exceeds 60 at % of Nb and one or more elements selected from among Mo, Al, Ge, and Ga.

The Ti-Nb-Mo based alloy of this embodiment will be described below. When adding Mo that is an element for stabilizing  $\beta$ -phase to a Ti-Nb based alloy, the temperature of  $\alpha/\beta$ -phase transformation point shifts to a lower temperature, and it is possible to obtain the alloy with stabilized  $\beta$ -phase even at room temperature. In other words, cooling the  $\beta$ -phase region rapidly enables the  $\beta$ -phase to remain.

In this embodiment, the content of Mo is 7at % or less. This is because of obtaining excellent workability. Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 7at % or less of Mo becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is easy in hot-working and cold-working .

The Ti-Nb-Al based alloy of this embodiment will be described below. When Al is added to Ti, it is considered that Al serves as an element for stabilizing  $\alpha$ -phase, the  $\alpha$ -phase region expands, and that the strength at RT increases. Therefore, in a composition with Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature and Al that is an element for stabilizing  $\alpha$ -phase, the martensite developing due to rapid cooling becomes thermo-elastic, thus obtaining  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity.

In this embodiment, the content of Al is 10at % or less. This is because of improving the workability. Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 10at % or less of Al becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working .

The Ti-Nb-Ge based alloy of this embodiment will be described below. When Ge is added to Ti, Ge serves as an element for stabilizing  $\alpha$ -phase. In this embodiment, the content of Ge is 6at % or less. This is because of improving the workability. Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 6at % or less of Ge becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, the alloy is thus easy in hot-working and cold-working .

The Ti-Nb-Ga based alloy of this embodiment will be described below. When Ga is added to Ti, Ga serves as an element for stabilizing  $\alpha$ -phase. In this embodiment, the content of Ga is 6at % or less. This is because of obtaining excellent workability. Accordingly, the Ti-based alloy containing 5 to 40at % of Nb and 6at % or less of Ga becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working .

The Ti-Nb-Mo-Al-Ga based alloy of this embodiment will be described below. When adding Nb that is an element for stabilizing  $\beta$ -phase and that decreases the martensitic transformation temperature, Mo that is an element for stabilizing  $\beta$ -phase and Al and Ga that serve each as an element for stabilizing  $\alpha$ -phase to Ti, the temperature of  $\alpha/\beta$ -phase transformation point shifts to a lower temperature, and it is possible to obtain the alloy with stabilized  $\beta$ -phase even at room temperature. In other words, cooling the  $\beta$ -phase region rapidly enables the  $\beta$ -phase to remain.

In this embodiment, the content of Mo is 7at % or less. This is because of obtaining excellent workability. The content of Al is 10at % or less. Also, this is because of obtaining excellent workability. The content of Ga is 6at % or less. Also, this is because of obtaining excellent workability.

Accordingly, the Ti-based alloy containing 5 to 40at % of Nb, 7at % or less of Mo, 10at % or less of Al, 6at % or less of Ge and 6at % or less of Ga becomes  $\beta$ -phase solid-solution Ti-based alloy with the superelasticity. Therefore, the crystal structure of the rapidly cooled Ti-based alloy is an orthorhombic system excellent in transformation ability, and the alloy is thus easy in hot-working and cold-working .

#### (Fourth embodiment)

The fourth embodiment of the present invention will be described specifically below. An alloy of this embodiment is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb, one or more elements selected from among 10at % or less of Mo, 15at % or less of Al, 10at % or less of Ge, 10at % or less of Ga and 15at % or less of In, 15at % or less of Sn, and Ti and unavoidable impurities as the residual part, where the sum total of one or more elements selected from among Mo, Al, Ge, Ga and In and Sn is 30at % or less, and the sum total of Nb, one or more elements selected from among Mo, Al, Ge, Ga and In, and Sn is 60at % or less.

The reason for adding Nb and one or more elements selected from among Mo, Al, Ge, Ga and In to Ti is to make the superelastic characteristic stable and excellent. Mo is an element which stabilizes  $\beta$ -phase and decreases the martensitic transformation temperature, as well as Nb. Added Al, Ge, Ga or In serves as an element for stabilizing  $\alpha$ -phase.

Sn serves as an element for stabilizing  $\alpha$ -phase, and makes the superelastic characteristic stable and excellent. In this embodiment, the content of Sn is 15at % or less. This is because the

content exceeding 15at % degrades the superelasticity, in other words, the alloy has plastic strain in deformation, and does return to the original state.

In addition, in this embodiment, the reasons for limiting respective ranges of the contents of Nb, Mo, Al, Ge, Ga and In conform to descriptions as in the second embodiment. Further, in this embodiment, the sum total of one or more elements selected from among Mo, Al, Ge, Ga and In and Sn is 30at % or less, and the sum total of Nb, one or more elements selected from among Mo, Al, Ge, Ga and In, and Sn is 60at % or less, the reasons for which also conform to descriptions as in the second embodiments.

(Fifth embodiment)

The fifth embodiment of the present invention will be described below. An alloy of this embodiment is a biomedical superelastic Ti-based alloy containing 5 to 40at % of Nb, one or more elements selected from among 7at % or less of Mo, 10at % or less of Al, 6at % or less of Ge, and 6at % or less of Ga, 12at % or less of Sn, and Ti and unavoidable impurities as the residual part, where the sum total of Nb, one or more elements selected from among Mo, Al, Ge and Ga, and Sn is 60at % or less.

The reason for adding Nb and one or more elements selected from among Mo, Al, Ge, and Ga to Ti is to make the superelastic characteristic stable and excellent. Mo is an element which stabilizes  $\beta$ -phase and decreases the martensitic transformation temperature, as well as Nb. Added Al, Ge, or Ga serves as an element for stabilizing  $\alpha$ -phase.

Sn serves as an element for stabilizing  $\alpha$ -phase, and makes the superelastic characteristic stable and excellent. In this embodiment, the content of Sn is 12at % or less. This is because of improving the workability.

In addition, in this embodiment, the reasons for limiting respective ranges of the contents of Nb, Mo, Al, Ge, and Ga conform to descriptions as in the third embodiment. Further, in this embodiment, the sum total of Nb, one or more elements selected from among Mo, Al, Ge and Ga, and Sn is 60at % or less, the reason for which also conforms to descriptions as in the third embodiment.

(Sixth embodiment)

The aforementioned biomedical superelastic Ti-based alloy according to this embodiment can be used for medical appliances such as a medical guide wire, orthodontic wire, stent, and actuator of an endoscope. Further, the alloy can be used for an eyeglass frame and nose pad arm of eyeglass. This is because the medical appliances do not cause allergy when used in contact with a human body, and are excellent in biocompatibility.

(Seventh embodiment)

The biomedical superelastic Ti-based alloy can be used as a medical guide wire, the reason for which is because the alloy has adequate superelastic characteristics and workability, and adequate biocompatibility.

(Eighth embodiment)

The biomedical superelastic Ti-based alloy can be used as an orthodontic wire, the reason for which is because the alloy has adequate superelastic characteristics and workability, and adequate biocompatibility.

(Ninth embodiment)

The biomedical superelastic Ti-based alloy can be used as a stent, the reason for which is because the alloy has adequate superelastic characteristics and workability, and adequate biocompatibility.

(Tenth embodiment)

The biomedical superelastic Ti-based alloy can be used as parts of eyeglass such as an eyeglass frame and nose pad arm of eyeglass, the reason for which is because the alloy has adequate superelastic characteristics and workability, and adequate biocompatibility.

(Eleventh embodiment)

The biomedical superelastic Ti-based alloy can be used as an actuator of an endoscope, the reason for which is because the alloy has adequate superelastic characteristics and workability, and adequate biocompatibility.

(Twelfth embodiment)

The development of superelasticity will be described briefly. Fig.6 is a schematic view illustrating conditions of development of superelasticity (refer to “Shape Memory Alloys”, HIROYASU FUNAKUBO., page 36).  $M_f$  indicates the temperature where transformation of austenite to martensite is finished.  $A_s$  indicates the austenite transformation start temperature, and  $A_f$  indicates the austenite transformation finish temperature.  $M_s$  indicates the temperature where transformation of austenite to martensite is started, and the line connecting  $M_s$  and  $M_d$  indicates the critical stress that generates stress-induced martensite.

Accordingly, when the critical stress for slip deformation is high as (A), the superelasticity develops in a stress-temperature range indicated by oblique lines below the critical stress. Fig.6 shows that the superelasticity does not develop when the critical stress against slip formation is low as (B). Further, Fig.6 shows that the superelasticity develops in a temperature range of  $A_s$  to  $M_d$ .

Since biomedical materials are used in or in contact with a human body, the usage temperature range thereof is near room temperature. Therefore, in order to obtain the superelasticity, it is required to control so that  $A_f$  is less than room temperature, and that  $M_d$  is sufficiently more than room temperature, for example, to an extent of body temperature. Generally,  $A_f$  is largely dependent on a composition of alloy, and is difficult to change with factors except the composition. Hence, it is desirable to control  $A_f$  by changing the component.

$M_d$  increases as the critical stress for slip deformation increases, and as  $M_d$  increases, more excellent superelasticity is obtained. In other words, in order to obtain excellent superelasticity, it is necessary to increase the critical stress for slip deformation.

As a method of increasing the critical stress for slip deformation, there is known a method of obtaining a worked structure where slip deformation is hard to occur. Also in Ti-based alloy, it is considered that the critical stress can be increased by performing cold working on the alloy to obtain a worked structure, and thereby making the structure where slip of dislocation is hard to take place.

The Ti-based alloy of the present invention is a  $\beta$ -stabilized Ti-based alloy, and has the  $\alpha$ -phase as a fine precipitation phase of the  $\beta$ -stabilized Ti-based alloy. As a method of increasing the critical stress for slip deformation, there is known a method of precipitating the  $\alpha$ -phase that is fine precipitation to prevent slip deformation.



The Ti-based alloy of the present invention is a  $\beta$ -stabilized Ti-based alloy, and has the  $\omega$ -phase as a fine precipitation phase of the  $\beta$ -stabilized Ti-based alloy. The precipitation of  $\omega$ -phase sometimes causes embrittlement. Therefore, in order to prevent the embrittlement from occurring, it is necessary to suppress the precipitation of  $\omega$ -phase as possible in heat treatment for providing the superelasticity.

As a result of studies on the foregoing, it is found out that a  $\beta$ -stabilized Ti-based alloy to which Nb is added is different from other  $\beta$ -stabilized Ti-based alloys, and that in such an alloy, precipitation of  $\omega$ -phase is a little even in heat treatment in a medium temperature range of 300 to 500°C, and at the same, the  $\alpha$ -phase precipitates in this temperature range. Further, it is found out that the  $\alpha$ -phase precipitates in a wider heat treatment temperature range, from 300 to 700°C, than the range of 300 to 500°C. Therefore, it is possible to maintain the critical stress for slip at a high level due to precipitation of  $\alpha$ -phase in heat treatment for providing the superelasticity, and to obtain the excellent superelasticity.

A method of manufacturing a biomedical superelastic Ti-based alloy is a method for preparing an ingot having a Ti-based alloy containing Ti and Nb, or the Ti-based alloy further containing one or more elements of Mo, Al, Ge, Ga and In and unavoidable impurities as the residual part, performing hot-working and cold-working on the ingot, performing annealing subsequent to the cold-working and further final cold-working with a processing rate of 20% or more, and performing heat treatment at a temperature of 300°C or more so as not to cause recrystallization or enlargement of crystal particle due to recrystallization.

In other words, also in the Ti-based alloy to which are added Nb and one or more elements of Mo, Al, Ge, Ga and In, by controlling the contents, the heat treatment in a medium temperature range of 300 to 500°C enables less precipitation of  $\omega$ -phase, and further enables precipitation of  $\alpha$ -phase at the same time in this temperature range. Accordingly, it is possible to precipitate the  $\alpha$ -phase in a wider heat treatment temperature range, from 300 to 700°C, than the range of 300 to 500°C. Thus, in the present invention is used the Ti-based alloy containing Ti and Nb, or the Ti-based alloy further containing one or more elements of Mo, Al, Ge, Ga and In.

The reasons for adding Mo, Al, Ge and Ga are because adding these elements enables increased strength, and improved superelastic characteristics. The reason for adding In is to obtain excellent workability.

Further, it is preferable in the present invention that a composition of the Ti-based alloy has 10 to 40at % of Nb, 10at % or less of Mo, 15at % or less of Al, 10at % or less of Ge, 10at % or less of Ga, and 15at % or less of In.

The reason why the lower limit of Nb that is an essential element is 10at % and the upper limit of Nb is 40at % is because the superelastic characteristic deteriorates when the content is out of the range. The reason why the upper limit of Mo is 10at %, upper limit of Al is 15at %, upper limit of Ge is 10at %, upper limit of Ga is 10at % and upper limit of In is 15at % is because when the limits exceed such values, the  $\omega$ -phase is precipitated much in the heat treatment, resulting in embrittlement.

In order to suppress precipitation of  $\omega$ -phase to prevent embrittlement, it is preferable that Mo is 3at % or less, Al is 5at % or less, Ge is 3at % or less, Ga is 3at % or less and In is 5at % or less.

Further, the sum total of one or more elements components selected from Mo, Al, Ge, Ga, and In is 30 at % or less. This is because the workability deteriorates when the sum total of one or more elements selected from Mo, Al, Ge, Ga, and In exceeds 30 at %.

The sum total of Nb that is the essential element, and one or more elements components selected from Mo, Al, Ge, Ga, and In is 60at % or less. This is because the superelasticity deteriorates when the sum total of Nb that is the essential element and one or more elements selected from Mo, Al, Ge, Ga, and In exceeds 60at %.

In the present invention, the cold-working rate after annealing is 20% or more. The 20% or more of cold-working rate after annealing is to prepare a worked structure where slip deformation is hard to occur, and a required worked structure is not obtained in rates of less than 20%. The upper limit of the cold-working rate is not determined particularly, and it is possible to perform the working of 70 to 80% in wire-drawing, and working of 90% or more in rolling.

In the present invention, the annealing is carried out at a temperature of 700°C or more that is sufficient for softening of materials. In terms of oxidation on the surface, the annealing may be carried out preferably in a temperature range of 700 to 900°C, more preferably, in a temperature range of 700 to 800°C, for a predetermined time. In the present invention, the annealing was carried out at 700°C for 10 minutes.

The heating temperature is 300°C or more. The reason for the temperature of 300°C or more is because the temperature of less than 300°C does not develop excellent superelasticity

even when the heat treatment is carried out for a long time. In particular, it is preferable to perform the heat treatment in a temperature range of 400 to 500°C. However, when the heat treatment is carried out at temperatures exceeding 500°C for a short time that does not cause recrystallization or that does not cause enlargement of crystal grains even in recrystallization, it is possible to maintain the critical stress for slip deformation at a high level and to obtain excellent superelasticity.

It is preferable to perform the heat treatment in a range of 1 minute to 2 hours. This is because the treatment of less than 1 minute results in insufficient heating and does not enable excellent superelasticity, and the treatment exceeding 2 hours degrades the efficiency.

The biomedical superelastic Ti-based alloy of the present invention is a Ti-based alloy which is obtained from the heat treatment at a heating temperature ranging from 400 to 500°C for a heating time ranging from 1 minute to two hours and which has residual strain of 1.5% or less after 4 % tensile elongation. This is because the strain exceeding 1.5% is large as residual strain and is difficult to use in medical appliances. In addition, the tensile test was carried out in accordance with JISH7103.

## Examples

The present invention will be described specifically below based on examples.  
(Example 1)

An ingot of Ti-Nb alloy with each composition as shown in Table 1 was cast after materials were melted by arc melting using a non-exhaust tungsten electrode in the Ar gas atmosphere. The obtained ingot was subjected to hot-working, and then to annealing and cold-drawing repeatedly, thereby manufacturing processed wire-rods each with a diameter of 1.0mm with a drawing rate after annealing of 40%. The annealing was carried out by performing the heat treatment at 700°C sufficient for softening of these materials for ten minutes. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. In addition, materials with low workability and with a processing rate after annealing of less than 40% were subjected to annealing the number of times more than that in the general case, and wire-rods each with a diameter of 1.0 mm were obtained.

Table 1

Composition and Shape Recovery Characteristic of Ti-Nb Alloy

No.	Composition (at%)		Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb			
A-1	balance	5	○	○	Example of Present Invention
A-2		10	○	○	
A-3		20	○	○	
A-4		30	○	○	
A-5		40	○	○	
A-6		0	○	×	Comparative Example
A-7		50	○	×	

In order to evaluate the shape recovery characteristic of each of the superelastic Ti-based alloy wire-rods, the wire-rod was wound around a stainless round bar with a diameter of 10mm to be bent once, and then held in a 180°-bent state for 30 seconds with the temperature of the wire-rod kept at 37°C, for example, by holding the wire-rod in a thermostatic chamber. The recovery characteristic was evaluated by twisting the wound wire off the stainless round bar and measuring a bent angle from the straight line.

A method of measuring a bent angle will be described with reference to Fig.1. Fig.1 shows an angle ( $\theta$ ) with respect to the horizontal plane which is a deformation degree of the superelastic Ti-based alloy 1 that was wound around the stainless round bar and did not return to the original shape of before being wound. With respect to the shape recovery characteristic, angles of 5° or less were “good”, and are indicated by O in the table, while angles exceeding 5° were “not good”, and are indicated by X in the table.

In order to evaluate the workability, annealing was performed on the processed wire-rod with a diameter of 1.0 mm at 700°C for 10 minutes, and cold-working was performed on the resultant until the wire-rod was broken and could not be drawn any more. The workability was evaluated using the maximum workable processing rate. With respect to the workability, wire-rods each with the maximum processing rate of 30% or more were regarded as being good in workability, and are indicated by O in the table. Wire-rods each with the maximum processing rate of less than 30% were regarded as being not good in workability, and are indicated by  $\Delta$  in the table. Wire-rods that could not be extended by even 1 mm were regarded as being bad in workability, and are indicated by X in the table.

Evaluation results on the workability and shape recovery characteristic are shown in Table 1. In Table 1, Nos.A-6 and A-7 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.A-1 to A-5 manufactured under conditions of the present invention returned to the original shape.

#### (Example 2)

With respect to Ti-Nb-Mo alloy with each composition as shown in Table 2, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give

superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 2.

Table 2

Composition and Shape Recovery Characteristic of Ti-Nb-Mo Alloy

No.	Composition (at%)			Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Mo			
B-1	balance	5	5	O	O	Example of Present Invention
B-2			7	O	O	
B-3			10	Δ	O	
B-4		20	5	O	O	
B-5			7	O	O	
B-6			10	Δ	O	
B-7		40	5	O	O	
B-8			7	O	O	
B-9			10	Δ	O	
B-10		20	15	Δ	x	Comparative Example
B-11		0	5	O	x	
B-12		50	5	O	x	

In Table 2, Nos.B-10 to B-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.B-1 to B-9 manufactured under conditions of the present invention returned to the original shape. Nos.B-1, B-2, B-4, B-5, B-7 and B-8 were better in workability than Nos.B-3, B-6 and B-9.

(Example 3)

With respect to Ti-Nb-Al alloy with each composition as shown in Table 3, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 3.



Table 3

Composition and Shape Recovery Characteristic of Ti-Nb-Al Alloy

No.	Composition (at%)			Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Al			
C-1	balance	5	5	○	○	Example of Present Invention
C-2			10	○	○	
C-3			15	△	○	
C-4		20	5	○	○	
C-5			10	○	○	
C-6			15	△	○	
C-7		40	5	○	○	
C-8			10	○	○	
C-9			15	△	○	
C-10		20	20	△	x	Comparative Example
C-11		0	5	○	x	
C-12		50	5	○	x	

In Table 3, Nos.C-10 to C-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.C-1 to C-9 manufactured under conditions of the present invention returned to the original shape. Nos.C-1, C-2, C-4, C-5, C-7 and C-8 were better in workability than Nos.C-3, C-6 and C-9.

(Example 4)

With respect to Ti-Nb-Ge alloy with each composition as shown in Table 4, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 4.

Table 4

Composition and Shape Recovery Characteristic of Ti-Nb-Ge Alloy

No.	Composition (at%)			Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Ge			
D-1	balance	5	3	O	O	Example of Present Invention
D-2			6	O	O	
D-3			10	Δ	O	
D-4		20	3	O	O	
D-5			6	O	O	
D-6			10	Δ	O	
D-7		40	3	O	O	
D-8			6	O	O	
D-9			10	Δ	O	
D-10		20	15	Δ	x	Comparative Example
D-11		0	3	O	x	
D-12		50	3	O	x	

In Table 4, Nos.D-10 to D-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.D-1 to D-9 manufactured under conditions of the present invention returned to the original shape. Nos.D-1, D-2, D-4, D-5, D-7 and D-8 were better in workability than Nos.D-3, D-6 and D-9.

(Example 5)

With respect to Ti-Nb-Ga alloy with each composition as shown in Table 5, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 5.

Table 5

Composition and Shape Recovery Characteristic of Ti-Nb-Ga Alloy

No.	Composition (at%)			Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Ga			
E-1	balance	5	3	O	O	Example of Present Invention
E-2			6	O	O	
E-3			10	Δ	O	
E-4		20	3	O	O	
E-5			6	O	O	
E-6			10	Δ	O	
E-7		40	3	O	O	
E-8			6	O	O	
E-9			10	Δ	O	
E-10		20	15	Δ	x	Comparative Example
E-11		0	3	O	x	
E-12		50	3	O	x	

In Table 5, Nos.E-10 to E-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.E-1 to E-9 manufactured under conditions of the present invention returned to the original shape. Nos.E-1, E-2, E-4, E-5, E-7 and E-8 were better in workability than Nos.E-3, E-6 and E-9.

(Example 6)

With respect to Ti-Nb-In alloy with each composition as shown in Table 6, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 6.

Table 6

Composition and Shape Recovery Characteristic of Ti-Nb-In Alloy

No.	Composition (at%)			Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	In			
F-1	balance	5	5	○	○	Example of Present Invention
F-2			12	○	○	
F-3			15	○	○	
F-4		20	5	○	○	
F-5			12	○	○	
F-6			15	○	○	
F-7		40	5	○	○	
F-8			12	○	○	
F-9			15	○	○	
F-10		20	20	○	×	Comparative Example
F-11		0	5	○	×	
F-12		50	5	○	×	

In Table 6, Nos.F-10 to F-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.F-1 to F-9 manufactured under conditions of the present invention returned to the original shape. Each of Nos.F-1 to F-12 was good in workability.

5 (Example 7)

With respect to Ti-Nb-Mo-Al alloy with each composition as shown in Table 7, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the  
10 wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 7.



Table 7

Composition and Shape Recovery Characteristic of Ti-Nb-Mo-Al Alloy

No.	Composition (at%)				Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Mo	Al			
G-1	balance	5	5	5	O	O	Example of Present Invention
G-2			7	10	O	O	
G-3			10	15	Δ	O	
G-4	balance	20	5	5	O	O	
G-5			7	10	O	O	
G-6			10	15	Δ	O	
G-7	balance	40	5	5	O	O	Comparative Example
G-8			7	10	O	O	
G-9			10	15	Δ	x	
G-10	balance	20	15	20	x	—	
G-11		0	5	10	O	x	
G-12		50	5	10	O	x	

In Table 7, Nos.G-9, G- 11 and G-12 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. No.G-10 with the composition out of the scope of the present invention was not good in workability, and could not be drawn even by 1mm. Therefore, the shape recovery characteristic could not be measured. In contrast thereto, Nos.G-1 to G-8 manufactured under conditions of the present invention returned to the original shape. Nos.G-1, G-2, G-4, G-5, G-7 and G-8 were better in workability than Nos.G-3 and G-6.

(Example 8)

With respect to Ti-Nb-Mo-Al-Ga alloy with each composition as shown in Table 8, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 8.

Table 8

Composition and Shape Recovery Characteristic of Ti-Nb-Mo-Al-Ga Alloy

No.	Composition (at%)					Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Mo	Al	Ga			
H-1	balance	5	5	5	3	O	O	Example of Present Invention
H-2			7	10	6	O	O	
H-3			10	10	10	Δ	O	
H-4		20		5	5	3	O	
H-5	7			10	6	O	O	
H-6	10			10	10	Δ	O	
H-7	30		5	5	3	O	O	
H-8			7	10	6	O	O	
H-9			10	10	10	Δ	O	
H-10	40		5	5	3	O	O	
H-11			10	15	10	×	—	
H-12			10	10	10	Δ	×	
H-13			0	5	6	6	O	
H-14	50		5	6	6	O	×	

In Table 8, Nos.H-12 to H-14 were not good in the superelastic characteristic because the compositions are out of the scope of the present invention, and did not return to the original shape. In contrast thereto, Nos.H-1 to H-10 manufactured under conditions of the present invention returned to the original shape. No.H-11 with the composition out of the scope of the present invention was not good in workability, and could not be drawn even by 1mm. Therefore, the shape recovery characteristic could not be measured. Nos.H-1, H-2, H-4, H-5, H-7, H-8 and B-10 were better in workability than Nos.H-3, H-6 and H-9.

(Example 9)

With respect to Ti-Nb-Mo-Sn alloy with each composition as shown in Table 9, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 9.

Table 9

Composition and Shape Recovery Characteristic of Ti-Nb-Mo-Sn Alloy

No.	Composition (at%)				Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Mo	Sn			
I-1	balance	5	5	5	O	O	Example of Present Invention
I-2			7	10	O	O	
I-3			10	15	Δ	O	
I-4	balance	20	5	5	O	O	
I-5			7	10	O	O	
I-6			10	15	Δ	O	
I-7	balance	40	5	5	O	O	Comparative Example
I-8			7	10	O	O	
I-9			10	10	Δ	O	
I-10	balance	20	10	15	Δ	x	
I-11			15	20	x	—	
I-12			5	10	O	x	
I-13	balance	50	5	10	O	x	

In Table 9, Nos.I-10, I-12 and I-13 with the compositions out of the scope of the present invention were not good in the superelastic characteristic, and did not return to the original shape. No.I-11 was not good in workability, and could not be drawn even by 1mm. Therefore, the shape recovery characteristic could not be measured. Nos.I-1 to I-9 manufactured under  
5 conditions of the present invention returned to the original shape. Nos.I-1, I-2, I-4, I-5, I-7 and I-8 were better in workability than Nos.I-3, I-6 and I-9.

(Example 10)

With respect to Ti-Nb-Mo-Al-Sn alloy with each composition as shown in Table 10, processed wire-rods each with a diameter of 1.0mm were manufactured using the same method  
10 as in Example 1. The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes with the shape held linearly. With respect to the wire-rods subjected to the shape memory heat treatment to give superelasticity, the workability and shape recovery characteristic were evaluated using the same method as in Example 1. The results are shown in Table 10.

Table 10

Composition and Shape Recovery Characteristic of Ti-Nb-Mo-Al-Sn Alloy

No.	Composition (at%)					Workability	Shape Recovery Characteristic	Remarks
	Ti	Nb	Mo	Al	Sn			
J-1	balance	5	5	5	5	O	O	Example of Present Invention
J-2			7	5	10	O	O	
J-3			10	5	15	Δ	O	
J-4	20		5	5	5	O	O	
J-5			7	5	10	O	O	
J-6			10	5	15	Δ	O	
J-7	40		5	5	5	O	O	Comparative Example
J-8			5	5	10	O	O	
J-9			10	5	15	Δ	x	
J-10	20		10	5	20	x	—	
J-11	0		5	5	10	O	x	
J-12	50		5	5	10	O	x	

In Table 10, Nos.J-9, J-11 and J-12 with the compositions out of the scope of the present invention were not good in the superelastic characteristic, and did not return to the original shape. No.J-10 was not good in workability, and could not be drawn even by 1mm. Therefore, the shape recovery characteristic could not be measured. Nos.J-1 to J-8 manufactured under conditions of the present invention returned to the original shape. Nos.J-1, J-2, J-4, J-5, J-7 and I-8 were better in workability than Nos.J-3 and J-6.

(Example 11)

Medical guide wires were manufactured for trial. An ingot of Ti-Nb(20at %)-Mo(5at %) alloy was melt and cast by ark melting a non-exhaust tungsten electrode in the Ar gas atmosphere and was subjected to hot-working, and then annealing and cold-drawing treatment repeatedly, thereby manufacturing wire-rods each with a diameter of 0.5mm with a cold-drawing rate of 40% after annealing.

The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes, and thereby the same materials as in B-4 in Table 2 were obtained. The tested wire-rods each with a diameter of 0.5mm were good in the superelastic characteristic and workability, provided with sufficient biocompatibility, and good when used as medical guide wires. A list of composition and results is shown in Table 11.



# Table 11

Processed Examples including Medical Appliances

Product Name	Composition (at%)			Diameter (mm)	Workability	Shape Recovery Characteristic
	Ti	Nb	Mo			
Medical Guide Wire	balance	20	5	0.5	○	○
Orthodontic Wire				0.5	○	○
Stent, Actuator of Endoscope				0.2	○	○
Eyeglass Frame, Nose Pad Arm of Eyeglass				2.0	○	○

(Example 12)

Orthodontic wires were manufactured by way of trial. An ingot of Ti-Nb(20at %)-Mo(5at %) alloy was melt and cast by ark melting using a non-exhaust tungsten electrode in the Ar gas atmosphere and was subjected to hot-working, and then annealing and cold-drawing repeatedly, thereby manufacturing wire-rods each with a diameter of 0.5mm with a cold-drawing rate of 40% after annealing.

The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes, and thereby the same materials as in B-4 in Table 2 were obtained. The tested wire-rods each with a diameter of 0.5mm were good in the superelastic characteristic and workability, provided with sufficient biocompatibility, and good when used as orthodontic wires. A list of composition and results is shown in Table 11.

(Example 13)

Products for use in a stent and actuator of an endoscope have the same diameter of 0.2mm, and therefore, were manufactured for trial at the same. An ingot of Ti-Nb(20at %)-Mo(5at %) alloy was melt and cast by ark melting using a non-exhaust tungsten electrode in the Ar gas atmosphere and was subjected to hot-working, and then annealing and cold-drawing repeatedly, thereby manufacturing wire-rods each with a diameter of 0.2mm with a cold-drawing rate of 40% after annealing.

The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes. The tested wire-rods were brought into coincidence with materials of B-4 in Table 2 in the cold processing rate after final annealing and temperature of the shape memory heat treatment to give superelasticity with a different diameter from that in B-4, and therefore were good in the superelastic characteristic and workability, provided with sufficient biocompatibility, and good when used as the stent and actuator of an endoscope. A list of composition and results is shown in Table 11.

(Example 14)

Eyeglass frames and nose pad arms of eyeglasses were manufactured by way of trial. An ingot of Ti-Nb(20at %)-Mo(5at %) alloy is prepared by ark melting using a non-exhaust tungsten electrode in the Ar gas atmosphere and the ingot was subjected to hot-working, and then

annealing and cold drawing repeatedly, thereby manufacturing wire-rods each with a diameter of 2.0 mm with a cold drawing rate of 40% after annealing.

The processed wire-rods were subjected to the shape memory heat treatment to give superelasticity at 500°C for 30 minutes. The tested wire-rods were brought into coincidence with materials of B-4 in Table 2 in the cold processing rate after final annealing and temperature of the shape memory heat treatment to give superelasticity with a different diameter from that in B-4, and therefore were good in the superelastic characteristic and workability, provided with sufficient biocompatibility, and good when used as eyeglass frames and nose pad arms of eyeglasses. A list of composition and results is shown in Table 11.

#### 10 (Example 15)

Materials were melt by ark melting using a non-exhaust tungsten electrode in the Ar gas atmosphere so as to obtain Ti-Nb alloy with Nb (27at %), and Ti and unavoidable impurities as the residual part, and an ingot of the alloy was cast and manufactured in a required form. The obtained ingot was subjected to hot-working, and then annealing and cold working repeatedly, thereby manufacturing wire-rods each with a diameter of 1.0mm with a processing rate of final cold working of 60%. For comparison, respective wire-rods with the final cold working rates of 10%, 20% and 40% were manufactured.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold processing rate, the respective materials with final cold processing rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 12. With respect to K-2 to K-10 under the present invention, residual strains had small values and were approximately 1.5% or less. With respect to comparative example K-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example K-1, since the heat-treatment temperature was low,

the residual strain was large. With respect to comparative example K-12, since the final cold working rate was 10% and thus low, the residual strain was large.

Table 12

## Ti-Nb Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
K-1	200	60	30	3.52	Comparative Example
K-2	300			1.38	Example of Present Invention
K-3	400	60	2	1.24	
K-4			5	1.19	
K-5			30	1.13	
K-6		40	30	1.23	
K-7	500	20	30	1.34	
K-8		60	30	1.22	
K-9	600			1.45	
K-10	700			1.50	
K-11	950	10	30	2.53	Comparative Example
K-12	400			2.78	

As an example of stress-strain curve, a curve for K-5 of an example of the present invention was shown in FIG.2. The vertical axis indicates the tensile stress (MPa), and the horizontal axis indicates the strain (%). The residual strain (1.13%) of K-5 is indicated by the arrow on the horizontal axis. A curve for comparative example K-11 subjected to the heat treatment is shown in FIG.3. The residual strain (2.53%) of K-11 is indicated by the arrow on the horizontal axis.

(Example 16)

Ti-Nb-Mo alloy with Nb (20at %), Mo(2at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold working of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold working, the respective materials with final cold working rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 13. With respect to L-2 to L-10 of examples of the present invention, residual strains had small values. With respect to comparative example L-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example L-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example L-12, since the final cold working rate was 10% and thus low, the residual strain was large.

Table 13

## Ti-Nb-Mo Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
L-1	200	60	30	3.10	Example of Present Invention
L-2	300			1.13	
L-3	400	60	2	0.64	
L-4			5	0.55	
L-5			30	0.42	
L-6		40	30	0.52	
L-7	500	20	30	0.75	
L-8		60	30	0.90	
L-9				1.21	
L-10				1.31	
L-11	950	10	30	2.12	Comparative Example
L-12	400			2.64	

(Example 17)

Ti-Nb-Al alloy with Nb (20at %), Al (3at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold working of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold working, the respective materials with final cold working rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 14. With respect to M-2 to M-10 of examples of the present invention, residual strains had small values. With respect to comparative example M-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example M-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example M-12, since the final cold working rate was 10% and thus low, the residual strain was large.



Table 14

Ti-Nb-Al Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
M-1	200	60	30	2.78	Example of Present Invention
M-2	300			1.23	
M-3	400	60	2	0.67	
M-4			5	0.61	
M-5			30	0.38	
M-6		40	30	0.50	
M-7		20	30	0.74	
M-8	500	60	30	0.77	
M-9	600			1.19	
M-10	700			1.29	
M-11	950			2.08	
M-12	400	10	30	2.43	Comparative Example

(Example 18)

Ti-Nb-Ge alloy with Nb (20at %), Ge (2at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold working of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold working rate, the respective materials with final cold working of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 15. With respect to N-2 to N-10 of example of the present invention, residual strains had small values. With respect to comparative example N-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example N-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example N-12, since the final cold working rate was 10% and thus low, the residual strain was large.

Table 15

## Ti-Nb-Ge Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
N-1	200	60	30	3.01	Example of Present Invention
N-2	300			1.20	
N-3	400	60	2	0.90	
N-4			5	0.84	
N-5			30	0.69	
N-6		40	30	0.72	
N-7	500	20	30	0.95	
N-8		60	30	0.88	
N-9	600			1.34	
N-10	700			1.44	
N-11	950			2.35	
N-12	400	10	30	2.76	Comparative Example

(Example 19)

Ti-Nb-Ga alloy with Nb (20at %), Ga (2at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold working rates of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold working rate, the respective materials with final cold working rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 16. With respect to O-2 to O-10 of examples of the present invention, residual strains had small values. With respect to comparative example O-11 subjected to solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example O-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example O-12, since the final cold drawing rate was 10% and thus low, the residual strain was large.

Table 16

## Ti-Nb-Ga Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
O-1	200	60	30	2.93	Example of Present Invention
O-2	300			1.21	
O-3	400	60	2	0.51	
O-4			5	0.49	
O-5			30	0.38	
O-6		40	30	0.50	
O-7	500	20	30	0.57	
O-8		60	30	0.82	
O-9	600			1.26	
O-10	700			1.37	
O-11	950	10	30	1.97	Comparative Example
O-12	400			2.35	

(Example 20)

Ti-Nb-In alloy with Nb (20at %), In (3at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold drawing rates of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold drawing rate, the respective materials with final cold drawing rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 17. With respect to P-2 to P-10 of examples of the present invention, residual strains had small values. With respect to comparative example P-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example P-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example P-12, since the final cold drawing rate was 10% and thus low, the residual strain was large.

Table 17

## Ti-Nb-In Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold-Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
P-1	200	60	30	3.46	Example of Present Invention
P-2	300			1.31	
P-3	400	60	2	1.09	
P-4			5	0.92	
P-5			30	0.88	
P-6		40	30	1.02	
P-7	500	20	30	1.14	
P-8		60	30	1.17	
P-9	600			1.42	
P-10	700			1.50	
P-11	950	10	30	2.21	Comparative Example
E-12	400			2.65	

(Example 21)

Ti-Nb-Mo-Al-Ga alloy with Nb (18at %), Mo (2at %), Al (3at %), Ga (2at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. Further, respective wire-rods with final cold working rates of 10%, 20% and 40% were manufactured as in Example 1.

The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 700°C. The heat-treatment time was 30 minutes. In addition, when the heat-treatment temperature was 400°C, the heat-treatment time was at 2 minutes and 5 minutes. Further, for comparison, the processed wire-rods were subjected to solution treatment at 950°C for 30 minutes. Furthermore, in order to check effects of the final cold working rate, the respective materials with final cold working rates of 10%, 20% and 40% were subjected to heat-treatment at 400°C for 30 minutes.

The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 18. With respect to Q-2 to Q-10 of examples of the present invention, residual strains had small values. With respect to comparative example Q-11 subjected to the solution treatment, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain. With respect to comparative example Q-1, since the heat-treatment temperature was low, the residual strain was large. With respect to comparative example Q-12, since the final cold working rate was 10% and thus low, the residual strain was large.



Table 18

## Ti-Nb-Mo-Al-Ga Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold- Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
					Comparative Example
Q-1	200	60	30	3.26	Example of Present Invention
Q-2	300			0.97	
Q-3	400	60	2	0.68	
Q-4			5	0.60	
Q-5			30	0.58	
Q-6		40	30	0.66	
Q-7	500	20	30	0.78	
Q-8		60	30	0.98	
Q-9				1.29	
Q-10				1.39	
Q-11	950	10	30	2.23	Comparative Example
Q-12	400			2.53	

(Example 22)

5 Ti-Mo-Al alloy with Mo (6at %), Al (7at %), and Ti and unavoidable impurities as the residual part was prepared, and processed wire-rods each with a diameter of 1.0mm were manufactured in the same way as in Example 1. The processed wire-rods were subjected to heat-treatment for every 100°C in a temperature range of 200 to 600°C. The heat-treatment time was 30 minutes.

10 The alloy wire-rods were subjected to the tensile test at room temperature, and residual strains after 4%-tensile are shown in Table 19. With respect to R-1 to R-3, since the heat-treatment temperature was low, the  $\omega$ -phase was precipitated, thereby causing embrittlement, and the material was broken with a strain of approximately 1%. With respect to R-4 and R-5, the heat-treatment temperature was high, and crystal grains were enlarged by recrystallization, resulting in a large residual strain.

Table 19

## Ti-Mo-Al Alloy

No.	Heat Temperature (°C)	Processing Rate of Final Cold- Working (%)	Heat Time (minutes)	Residual Strain (%)	Remarks
R-1	200	60	30	—	Comparative Example
R-2	300			—	
R-3	400			—	
R-4	500			1.88	
R-5	600			1.77	

### Industrial Applicability

By adding Nb, adding Nb and one or more elements of Mo, Al, Ge, Ga and In, or further adding Sn in a suitable amount to Ti, it is possible to cause the superelastic effect to develop.

Further, by performing suitable heat treatment on a Ti-based alloy containing Nb, or a Ti-based  
5 alloy containing Nb and one or more elements of Mo, Al, Ge, Ga and In, it is possible to cause the excellent superelastic effect to develop.

All of Ti, Nb, Mo, Al, Ge, Ga, In and Sb are elements safe to a living body. The alloys of the present invention comprised of the elements do not contain Ni, and therefore, do not have any concerns about allergy, and are suitable for use in living bodies.